Reflection electron energy loss spectroscopy during initial stages of Ge growth on Si by molecular beam epitaxy

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Using a conventional reflection high-energy electron diffraction gun together with an electron energy loss spectrometer, we have combined *in situ* measurements of inelastic scattering intensities from Si $L_{2,3}$ and Ge $L_{2,3}$ core losses with reflection electron diffraction data in order to analyze the initial stages of Ge heteroepitaxy on Si(001). Diffraction data indicate an initial layer-by-layer growth mode followed by island formation for Ge thicknesses greater than 0.8–1.1 nm. The electron energy core loss data are consistent with a simple model of grazing incidence electron scattering from the growing Ge film. Reflection electron energy loss spectroscopy is found to be highly surface sensitive, and the energy resolution and data rate are also sufficiently high to suggest that reflection electron energy loss spectroscopy may be a useful real-time, *in situ* surface chemical probe during growth by molecular beam epitaxy.

The precise dimensional control and low growth temperatures of modern epitaxial growth techniques have made it possible to tailor compositionally modulated thin films on an atomic level. A significant factor currently limiting far greater insight about and control of epitaxial growth is a relative lack of *in situ* chemical analysis techniques which are compatible with the requirements of typical growth environments, such as long working distance and compatibility with deposition sources. The most widely employed *in situ* probe for molecular beam epitaxy, reflection high-energy electron diffraction (RHEED), is sensitive to surface crystallographic structure and morphology, but does not provide direct measurements of surface composition. Several approaches have been taken to surface compositional analysis during growth, such as reflection mass spectrometry[1] and ellipsometry.[2] Each of these techniques is an indirect indication of surface composition. Another approach is reflection electron energy loss spectrometry, which is a direct probe of surface composition, since electrons inelastically scattered from the surface are spectroscopically analyzed.

Electron energy loss spectrometry in the transmission electron microscope has become an important analytic tool complementary to imaging and diffraction and has typically been done in transmission geometry.[3] Moreover, analysis of extended electron loss fine structure has made possible investigations of local order in solids which were previously confined to intense x-ray source facilities, such as a synchrotron.[4] Experiments conducted in a transmission electron microscope have demonstrated that electron energy loss spectrometry is also possible in reflection mode.[5,6] Other experiments using a low-energy electron source in a surface analysis system, demonstrated the use of electron energy loss spectroscopy in the analysis of Cu growth on Ag(111).[7] In this letter, we introduce the use of reflection electron energy loss spectrometry (REELS) as an *in situ* technique for analysis of crystal growth in a conventional molecular beam epitaxy system using a RHEED electron beam source, and discuss application to Ge heteroepitaxy on Si.

The scattering configuration employed for REELS in the present work is similar to a conventional RHEED configuration, with an electron beam incidence angle of $\phi = 37$ mrad. Structural analysis by RHEED at 30 keV with an emission current of 30 μA was performed simultaneously with the REELS measurements. The RHEED screen was viewed in reflection, and a 3 mm aperture in the RHEED screen formed the entrance to the electron energy loss spectrometer. The spectrometer is a Gatan 607 second-order corrected sector identical to that normally used in a transmission electron microscope. The object point of the spectrometer is the sample itself, located $\sim$33 cm from the spectrometer entrance, giving a collection semiangle of 5 mrad. The spectrometer energy resolution, calculated at 25 keV using the first-order matrix coefficients[8] for this sector and an assumed 90 μm beam waist, is $\sim$5 eV. Assuming an incident thermal beam spread of 1.5 eV, and high voltage power supply resolution of 3 eV, the energy resolution of the system is expected to be $\sim$6 eV. Experimental measurements of the energy width of the through beam (i.e., the beam which does not strike the sample) indicated a system resolution of $\sim$7 eV. While this is not a high-energy resolution, it is more than adequate for quantitative analysis of core losses.

Initial experiments concentrated on characterizing the optimum scattering geometry for observation of core loss edge intensities for Si and Ge substrates. Several diffraction conditions were investigated: (i) specular reflection coincident with a Bragg peak of the substrate (in-phase), (ii) specular reflection not coincident with a substrate Bragg peak (out-of-phase), and (iii) a surface resonance condition, where the out-of-phase specular reflection intensity

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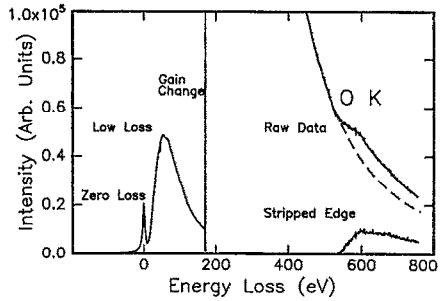

FIG. 1. REELS spectrum illustrating O K edge from $\simeq 3$ nm native SiO_2 on Si (001) after sample insertion, and before SiO_2 desorption by heating.

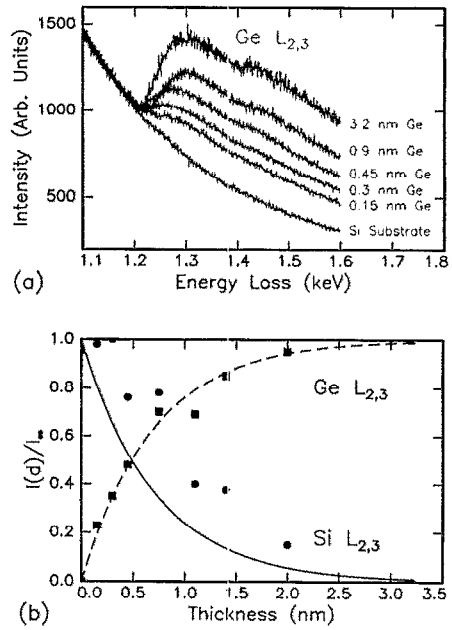

FIG. 2. REELS spectra illustrating change in Ge $L_{2,3}$ edge intensity with Ge thickness shown in (a); variation of normalized Ge $L_{2,3}$ and Si $L_{2,3}$ intensities with coverage shown in (b).

was enhanced by coincidence of an oblique Kikuchi line with the specular beam spot.[9,10] For Ge substrates, the Ge $L_{2,3}$ edge was observable in all three conditions, however better ratios of edge intensity to inelastic background intensity were obtained for conditions (ii) and (iii). It has been reported by Wang *et al.* that condition (iii) scattering, corresponding to surface resonance, is required to obtain acceptable ratios of core loss intensity to inelastic background intensity.[6] Little difference was observed in the ratio of edge intensity to inelastic background between conditions (ii) and (iii) above in the present work. However, it was determined qualitatively that surface sensitivity is strongly enhanced by adoption of surface resonant scattering conditions. For example, after growth of 0.3–0.5 nm of Si on a Ge (001) substrate, the Ge $L_{2,3}$ core loss intensity from the substrate was not observable. For nonresonant conditions, the substrate core loss intensity is still observable after growth of a 2.0–3.0 nm thick overlayer, as discussed below.

Films were grown in a custom-designed molecular beam epitaxy system, which is equipped with electron beam sources for deposition of Si and Ge. Although our growth chamber normally achieves base pressures of 1×10^{-10} Torr, addition of the electron energy loss spectrometer, which is not of ultrahigh vacuum design in its current configuration, resulted in base pressures of 5×10^{-9} Torr with pressure rising to $1\text{–}2\times10^{-8}$ Torr during deposition. The Si buffer layers and Ge films were epitaxial, but transmission electron microscopy indicated stacking faults in the Si buffer layers for some samples.

After insertion into the growth chamber, Si (001) substrates were coated with a thin native SiO_2 layer, judged to be $\leqslant 3$ nm thick since this layer was desorbed prior to Si buffer layer growth by briefly heating the substrate to 800 °C. Before desorption, the RHEED pattern consisted of broad, strongly modulated streaks, and no surface reconstruction was visible. In these conditions, the O K edge is clearly visible in the reflection electron energy loss spectrum, as shown in Fig. 1.

Following growth of a 300 nm Si buffer layer on a Si (001) substrate, a streaked RHEED pattern with the Si 100-(2×1) reconstruction characteristic of clean surfaces was observed. Ge was grown at a rate of 0.84 nm/min on (001) Si substrates at a temperature of 410 °C. Film thickness was measured using quartz crystal sensors which had been previously calibrated using Rutherford backscattering spectrometry. Growth was briefly interrupted to collect electron energy loss spectra. Energy loss spectra taken in scattering condition (ii) are shown in Fig. 2(a) as a function of Ge thickness. The collection time for each spectrum was 40 s. The appearance of the Ge $L_{2,3}$ edge is clearly visible in the electron energy loss spectrum at Ge thicknesses as small as 0.15 nm. For Ge thicknesses $d\geqslant 0.3$ nm, the Ge L_1 edge is also visible. It should be emphasized that the results in Fig. 2(a) are data from single spectra, and have not been averaged or otherwise processed, except to normalize the pre-edge background intensity. We expect the pre-edge intensity to remain constant, since the scattering geometry was unchanged during film growth. The variation of the core less intensities with nominal Ge film thickness for the Ge $L_{2,3}$ edge (film) and the Si $L_{2,3}$ edge (substrate) is shown in Fig. 2(b).

Also for $d\geqslant 0.3\text{–}0.4$ nm, the RHEED pattern consisted of sharp spots characteristic of diffraction from a rough surface. The change in the RHEED pattern was interpreted as marking the onset of islanding, which is consistent with other observations of Ge heteroepitaxy on Si that indicate a Stranski–Krastanov growth mode.[11,12] This conclusion was checked by *ex situ* reflection electron microscopy and cross-sectional transmission electron microscopy, performed in a Philips EM-430 microscope. Figure 3 is a transmission electron micrograph taken along the [011] zone axis of Ge islands on Si (001) for a sample with a nominal coverage of $d = 3.2$ nm Ge on Si. For this sample, Ge islands were approximately 15–30 nm in diameter, with an average interisland distance of $\sim$50–100 nm. The island contact angle on the substrate was $\sim 65°$.

The normalized Ge $L_{2,3}$ and Si $L_{2,3}$ intensities shown in Fig. 2 were determined from power law background fits for

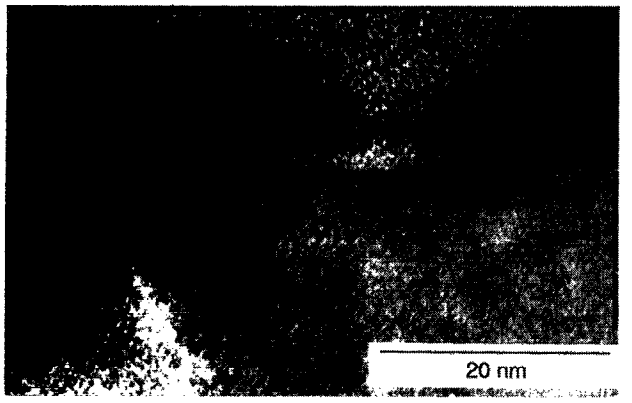

FIG. 3. High-resolution cross-sectional electron micrograph of Ge islands on Si (001) for a sample with nominal thickness of 3.2 nm Ge grown at $T = 410$ °C.

200 eV windows. These intensities vary gradually and in a complementary manner with coverage in the range $0 < d < 3.2$ nm. For nonresonant conditions, it is possible to interpret the changes in intensities with coverage as being due to electron energy loss at grazing incidence angle ϕ from thin uniform overlayer of thickness d, which is in most respects very similar to transmission electron energy loss, with a core loss scattering yield I_c from an elemental overlayer given by

$$I_c = I(\Delta E)\sigma(\Omega,\Delta E)N_{\rm el}[\lambda(1 - e^{-d/\sin\phi\lambda})], \qquad (1)$$

where $I(\Delta E)$ is the integrated low-loss intensity, and $N_{\rm el}$ is the elemental concentration of a given species in the overlayer. The integrated elemental scattering cross section, $\sigma(\Omega,\Delta E)$ is dependent on the collection semiangle Ω, and the energy loss window for data collection ΔE. The effective thickness for electron scattering is equal to the projected overlayer thickness $d/\sin\phi$ for very thin overlayers of uniform thickness. In thicker overlayers, the effective thickness is limited by λ, the mean free path for total electron scattering. The solid line and dashed line in Fig. 2(b) are the intensities predicted using this simple transmission model for Si and Ge, respectively, assuming a uniform film thickness, and an electron mean free path at an energy of 30 keV of $\lambda \simeq 20$ nm.[13] Excellent agreement is obtained between the theoretical and experimental intensities for the Ge $L_{2,3}$ edge. The agreement between theoretical and experimental intensities for the Si $L_{2,3}$ edge is not as good, possibly due to multiple inelastic scattering in the low-loss region, resulting in less accurate background fits. At an incidence angle of $\phi = 37$ mrad, the actual film thickness at which the projected thickness is equal to the total mean free path is $d = 0.74$ nm. Since Ge growth on Si results in island formation, a more refined analysis could be developed which accounts for the geometrical differences in scattering from an overlayer of uniform thickness and one consisting of islands. However, for the parameters of this experiment (e.g., island density, island contact angle, electron mean free path, beam incidence angle), these geometrical differences are expected to be minor.

In conclusion, we have introduced reflection electron energy loss spectroscopy as an *in situ* probe of surface composition during molecular beam epitaxy, and have applied the technique to the study of Ge growth on Si (001). Core loss intensities are observable in thin overlayers for surface resonant as well as nonresonant conditions. The changes in relative intensities of Ge $L_{2,3}$ and Si $L_{2,3}$ core losses from a Ge overlayer on a Si substrate are consistent with a simple model of grazing incidence electron scattering. Considerable work remains to be done in assessing the resonance enhancement of surface sensitivity, as well as absolute and relative chemical sensitivity in order to develop reflection electron energy loss spectroscopy for more general growth conditions (e.g., growth of compound materials). Considerable gains in data rate for deep core losses could also be realized by use of an electron energy loss spectrometer with parallel detection. Nonetheless, these initial experiments have demonstrated that the surface sensitivity, data rate, and energy resolution are sufficiently high to suggest that reflection electron energy loss spectroscopy has great potential as a practical real time, *in situ* probe of surface composition during epitaxial growth.

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